HYDROCHEMICAL STABILITY OF A DROP IN THE MASS TRANSFER OF SURFACTANTS

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It is known that the mass transfer of substances capable of changing surface tension and interphase chemical reactions may lead to the development of surface-tension gradients. As a result of the Marangoni effect [1], these gradients can result in instability of the phase boundary and lead to the formation of near-surface convection structures, as well as to the development of interphase convection and turbulence within the phases [2]. The study of the hydrodynamic stability of a reacting liquid drop surrounded by a gas or another immiscible liquid is of special interest in connection with the problem of intensifying mass transfer processes in the chemisorption of gases and in liquid extraction accompanied by chemical reactions [3].

The problem of the stability of a spherical phase boundary (the surface of a drop or bubble) in the presence of surface reactions and the transfer of surfactants was examined in the most general form in [4, 5]. The study [4] presented a linear analysis of the stability of the steady state, with allowance for an arbitrary number of reacting substances and chemical reactions on the surface. The dependence of the rates of these reactions on concentration was described by a general function, a dispersion relation was obtained, and this relation was analyzed in a small-drop approximation for a single reacting substance. Here, a detailed examination was made of the deformational stability of the drop surface. The results of this work were generalized in [5], where, under the condition of local adsorptive equilibrium between the phase boundary (interface) and the adjacent layer of liquid, the authors considered the convective diffusion of the reactants in the phases.

Here, along with the phenomena considered previously, we examine the effect of surfactant adsorption at a finite rate on the hydrodynamic stability of a drop. This case contrasts with the case examined in the previous investigations, where the adsorption rate was assumed to be infinitely large. We gave special attention to the onset of instability and to finding critical values of dimensionless parameters characterizing the rate of the interfacial chemical reaction and the surface activity of the reactants being transported.

1. We will examine a drop of liquid immersed in an infinite, homogeneous, quiescent liquid that does not mix with the first liquid. In each phase, we dissolve a substance which has surface-active properties and which does not dissolve in the other phase. Diffusion brings the substances to the interface, where they are adsorbed and react with one another. The rate of adsorption and desorption of the respective substances at the interface is comparable with the rate of the chemical reaction and the rate at which diffusion transports the substances to the interface. The reaciton products do not have surface-active properties and are rapidly (compared to the adsorption of the surfactants) removed from the phase boundary. The reaction being examined belongs to a broad class of interfacial reactions in which thermal effects are very slight [6]. Thus, in studying the dynamics of the phase boundary, we will ignore thermocapillary effects compared to concentration-capillary effects caused by the dependence of surface tension on the concentration of the reactants. Here, we make allowance for the effects associated with the presence of surface viscosity and the inertia of the adsorbed surfactants, since these effects play a significant role in the kinetics of certain interfacial reactions [7].

We choose a spherical coordinate system with its origin at the center of mass of the drop. The steady-state concentrations of the reactants in the undisturbed system will be assumed to have a spherically symmetrical distribution in conformity with the law $C_1 = C_{10}(1 - a_1 r^{-n_1})$, $C_2 = C_{20}(1 - a_2 r^{n_2})$, where C_i is the concentration of reactants in the volumes of the phases; r is the radial coordinate; C_{i0} (i = 1, 2) is the concentration of the reactants at infinity and at the center of the drop, respectively; a_i, $n_i > 0$ are constants; the subscript i = 1 pertains to the external liquid, while i = 2 pertains to the liquid of the drop. Such concentration distributions are solutions of the steady-state equations: a)

$\Delta C_i = 0$ ($n_1 = 1$, $n_2 = 0$), b) $\Delta C_i = Q_i = \text{const}$ ($-n_1 = n_2 = 2$), c) $\Delta C_1 = 0$, $\Delta C_2 = Q$ ($n_1 = 1$, $n_2 = 2$). Case "b," corresponding to the formation of surface-active reactants in the volumes of the phases due to the presence of stationary, uniformly-distributed sources (such as sources resulting from a zeroth-order bulk reaction), was examined in [5]. In case "c," the surfactant is formed inside the drop as a result of a zeroth-order reaction, while sources are absent outside the drop. For other values of the exponents n_1 and n_2, the stationary concentration profiles being examined can serve as approximations of the actual concentration distributions corresponding to volumetric sources or sinks of another type. The thus-chosen concentration distributions for the reacting surfactants make it possible to determine the effect of the stationary concentration profiles on the character of stability of the system. The drop surface will be assumed to be spherical and undeformable (the surface tension σ is great). Here, by the stability of the phase boundary, we mean stability against the formation of near-surface convective motions of the liquid.

Study of the hydrodynamic stability of a drop involves the solution of a stability problem concerning infinitesimal perturbations of the velocity of the liquid flow and the concentrations of surfactants dissolved in both phases and adsorbed on the interface.

The velocity perturbations are described in the chosen spherical coordinate system by dimensionless linearized Navier–Stokes equations, the equations of continuity of the flow, and boundary conditions expressing impermeability and the absence of slip at the interface:

$$\frac{\partial u_i}{\partial t} = -\frac{\partial p_i}{\partial r} + R_i^{-1}\left(\Delta u_i - \frac{2}{r^2} u_i - \frac{2}{r^2 \sin\theta}\frac{\partial(v_i \sin\theta)}{\partial\theta} - \frac{2}{r^2 \sin\theta}\frac{\partial w}{\partial\varphi}\right); \tag{1.1}$$

$$\frac{1}{r^2}\frac{\partial}{\partial r}(r^2 u_i) + \frac{1}{r\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta v_i) + \frac{1}{r\sin\theta}\frac{\partial w_i}{\partial\varphi} = 0; \tag{1.2}$$

$$u_1 = u_2 = 0, \quad v_1 = v_2, \quad w_1 = w_2 \quad \text{at} \quad r = 1, \tag{1.3}$$

$$t = t'/\tau, \quad r = r'/a, \quad (u_i, v_i, w_i) = (u_i'\tau/a,$$

$$v_i\tau/a, \; w_i\tau/a), \quad p_i = p_i'\tau^2/\rho_i a^2, \quad R_i = a^2/\nu_i\tau.$$

Here, t' is time; r' is the radial coordinate; u_i', v_i', and w_i' are components of velocity with respect to $(r', \theta, \varphi$; ρ_i', p_i' are density and pressure; ν_i is the kinematic viscosity; τ is the characteristic time of surface chemical reaction; a is the radius of the drop. The equations for the remaining velocity components are not written because the problem reduces to the solution of the equation for the radial component of velocity.

The perturbations of the bulk and surface concentrations are described by linearized equations of convective diffusion in the volume of the phases and the balance of the adsorbed substance on the drop surface, as well as by the balance condition for the diffusive and adsorptive flows at the interface:

$$\frac{\partial z_i}{\partial t} + u_i \frac{\partial z_{i0}}{\partial r} = \chi_i^{-1}\Delta z_i; \tag{1.4}$$

$$\frac{\partial\gamma_i}{\partial t} + \gamma_{i0}\left(\frac{1}{\sin\theta}\frac{\partial}{\partial\theta}(\sin\theta v_1) + \frac{1}{\sin\theta}\frac{\partial w_1}{\partial\varphi}\right) = \chi_{si}^{-1}L^2\gamma_i - \sum_{j=1,2}f_{ij}\gamma_j + \sum_{j=1,2}b_{ij}\gamma_j + b_{iz}z_i; \tag{1.5}$$

$$d_i(-1)^i\frac{\partial z_i}{\partial r} = \sum_{j=1,2}b_{ij}\gamma_j + b_{iz}z_i, \tag{1.6}$$

$$z_i = -C_i/C_{i0}, \quad \gamma_i = \Gamma_i/\Gamma_i^*, \quad \chi_i = a^2/D_i\tau,$$

$$\chi_{si} = a^2/D_{is}\tau, \quad d_i = D_i\tau C_{i0}/a\Gamma_i^* = (C_{i0}a/\Gamma_i^*)\chi_i^{-1},$$

$$f_{ij} = \frac{\tau}{\Gamma_i^*}\left[\frac{\partial}{\partial\gamma_j}F_i(C_i, \Gamma_1, \Gamma_2)\right]_0,$$

$$b_{ij} = \frac{\tau}{\Gamma_i^*}\left[\frac{\partial}{\partial\gamma}J_i(C_i, \Gamma_1, \Gamma_2)\right]_0, \quad b_{iz} = \frac{\tau}{\Gamma_i^*}\left[\frac{\partial}{\partial z_i}J_i(C_i, \Gamma_1, \Gamma_2)\right]_0,$$

$$\Delta = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial^2}{\partial\varphi^2},$$

$$L^2 = \Delta - \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right).$$

Here, C_i are the perturbations of the concentrations of the reactants in the i-th phase; Γ_i is the surface concentration of the i-th reactant; Γ_i^* is the limiting surface concentration; D_i and D_{si} are the bulk and surface diffusion coefficients; $F_i(\Gamma_1, \Gamma_2)$ and $J_i (C_i, \Gamma_1, \Gamma_2)$ are functions which describe the kinetics of surface chemical reaction and adsorption; the subscript 0 denotes the steady state.

The perturbations of flow velocity and surface concentration must satisfy balance conditions for the normal and tangential components of the stresses at the interface, with allowance for the Marangoni effect, surface viscosities, and the inertia of the adsorbed substance [8]. Since the interfacial tension is large and the drop is assumed to be unde-formable, the condition for the normal stresses reduces to a pressure jump at the interface. The balance conditions for the shear stresses take the form

$$\gamma_0 \frac{\partial v_1}{\partial t} = m_1 \left(\frac{\partial u_1}{\partial \theta} + \frac{\partial v_1}{\partial r} - v_1 \right) - m_2 \left(\frac{\partial u_2}{\partial \theta} + \frac{\partial v_2}{\partial r} - v_2 \right) + M_1 \frac{\partial \gamma_1}{\partial \theta} + \tag{1.7}$$

$$+ M_2 \frac{\partial \gamma_2}{\partial \theta} + \varkappa_1 \frac{\partial}{\partial \theta} \left\{ \frac{1}{\sin \theta} \left[\frac{\partial}{\partial \theta} (v_1 \sin \theta) + \frac{\partial w_1}{\partial \varphi} \right] \right\} +$$

$$+ \varkappa_2 \left\{ 2v_1 + \frac{1}{\sin \theta} \frac{\partial}{\partial \varphi} \left[\frac{1}{\sin \theta} \left(\frac{\partial v_1}{\partial \varphi} - \frac{\partial}{\partial \theta} (w_1 \sin \theta) \right) \right] \right\};$$

$$\gamma_0 \frac{\partial w_1}{\partial t} = m_1 \left(\frac{\partial w_1}{\partial r} + \frac{1}{\sin \theta} \frac{\partial u_1}{\partial \varphi} - w_1 \right) - m_2 \left(\frac{\partial w_2}{\partial r} + \frac{1}{\sin \theta} \frac{\partial u_2}{\partial \varphi} - w_2 \right) + \tag{1.8}$$

$$+ \frac{1}{\sin \theta} \left(M_1 \frac{\partial \gamma_1}{\partial \varphi} + M_2 \frac{\partial \gamma_2}{\partial \varphi} \right) + \varkappa_1 \frac{1}{\sin \theta} \frac{\partial}{\partial \varphi} \left\{ \frac{1}{\sin \theta} \left(\frac{\partial}{\partial \theta} (v_1 \sin \theta) + \frac{\partial w_1}{\partial \varphi} \right) \right\} +$$

$$+ \varkappa_2 \left\{ 2w_1 - \frac{\partial}{\partial \theta} \left[\frac{1}{\sin \theta} \left(\frac{\partial v_1}{\partial \varphi} - \frac{\partial}{\partial \theta} (w_1 \sin \theta) \right) \right] \right\},$$

$$m_i = \frac{\eta_i \tau}{a \Gamma_1^*}, \quad \varkappa_1 = \frac{(k + \varepsilon) \tau}{a^2 \Gamma_1^*}, \quad \varkappa_2 = \frac{\varepsilon \tau}{a^2 \Gamma_1^*},$$

$$M_i = \frac{\partial \sigma}{\partial \Gamma_i} \frac{\tau^2}{a^2} \frac{\Gamma_i^*}{\Gamma_1^*}, \quad \gamma_0 = \frac{\Gamma_{10} + \Gamma_{20}}{\Gamma_1^*}, \quad \frac{\partial \sigma}{\partial \Gamma_i} = \text{const},$$

where η_i are the bulk viscosities; k and ε are the surface dilatational and shear viscosities; M_i are the Marangoni numbers.

2. Using continuity equation (1.2), we can rewrite Eq. (1.1) as follows:

$$\partial u_i / \partial t = - \partial p_i / \partial r + R_i^{-1} r^{-1} \Delta (r u_i). \tag{2.1}$$

Since pressure is a harmonic function in the linearized Navier–Stokes equation (which does not contain convective terms), we have the following, with allowance for the conditions of boundedness inside the drop and at infinity:

$$p_1 = \sum_{l=0}^{\infty} a_{1l} r^{-l-1} Y_l (\theta, \varphi) e^{\omega_l t}, \tag{2.2}$$

$$p_2 = \sum_{l=0}^{\infty} a_{2l} r^l Y_l (\theta, \varphi) e^{\omega_l t}, \quad Y_l (\theta, \varphi) = \sum_{m=-l}^{m=l} b_{ml} Y_l^m (\theta, \varphi)$$

$\left(Y_l^m (\theta, \varphi) \right.$ are spherical functions, b_{ml}, a_{il} ($i = 1, 2$) are arbitrary constants).

We seek a solution of (2.1) in the form

$$u_i = \sum_{l=1}^{\infty} r^{-1} U_{il} (r) Y_l (\theta, \varphi) e^{\omega t}. \tag{2.3}$$

Here, the mode with the number $l = 0$ is not considered, since the liquids are immiscible. For the sake of brevity, the subscript l with ω will be dropped.

Inserting (2.2) and (2.3) into (2.1), we obtain equations for U_{il}. The solutions of these equations, bounded at the center of the drop and approaching zero at infinity, will be written in the form

$$U_{1l} = A_{1l} r^{-l-1} + B_{1l} K_{l+1/2}^* (q_1 r), \quad U_{2l} = A_{2l} r^l + B_{2l} I_{l+1/2}^* (q_2 r), \tag{2.4}$$

$$I_{l+1/2}^* (x) = (\pi/2x)^{1/2} I_{l+1/2} (x), \quad K_{l+1/2}^* (x) = (\pi/2x)^{1/2} K_{l+1/2} (x),$$

where $I_{\ell+1/2}(x)$, $K_{\ell+1/2}(x)$ are modified spherical Bessel functions of the first and second kind [9]; $A_{i\ell}$ and $B_{i\ell}$ are arbitrary constants. Using the continuity equation (1.2), boundary conditions (1.3), and the recursion formulas for the functions $I^*_{\ell+1/2}(x)$ and $K^*_{\ell+1/2}(x)$, we find

$$A_{1l} + B_{1l}K^*_{l+1/2}(q_1) = 0, \quad A_{2l} + B_{2l}I^*_{l+1/2}(q_2) = 0,$$
$$B_{1l}q_1K^*_{l-1/2}(q_1) + B_{2l}q_2I^*_{l+3/2}(q_2) = 0. \tag{2.5}$$

Let us examine Eq. (1.4). We will assume that $z_{i0} = a_1r^{-n_1}$, $z_{20} = a_2r^{n_2}$, $n_1 > 0$, $n_2 > 0$. We seek the solution of (1.4) in the form

$$z_i = \sum_{l=1}^{\infty} Z_{il}(r) Y_l(\theta, \varphi) e^{\omega t}. \tag{2.6}$$

Then, for $Z_{i\ell}$, we obtain equations with solutions that are bounded at the center of the drop and approach zero at infinity:

$$Z_{1l}(r) = C_{1l}K^*_{l+1/2}(s_1r) + B_{1l}\beta_{1l}(s_1) I^*_{l+1/2}(s_1r) + \zeta_{1l}(r), \tag{2.7}$$
$$Z_{2l}(r) = C_{2l}I^*_{l+1/2}(s_2r) + B_{2l}\beta_{2l}(s_2) K^*_{l+1/2}(s_2r) + \zeta_{2l}(r);$$

$$\zeta_{il}(r) = I^*_{l+1/2}(s_ir) \int_1^r W^{-1}K^*_{l+1/2}(s_ir) h_i(r) dr - \tag{2.8}$$

$$- K^*_{l+1/2}(s_ir) \int_1^r W^{-1}I^*_{l+1/2}(s_ir) h_i(r) dr, \quad \zeta_{il} = d\zeta_{il}/dr = 0, \quad r = 1;$$

$$\beta_{1l}(s_1) = \chi_1 a_1 n_1 s_1^{n_1} \int_{s_1}^{\infty} t^{-n_1}K^*_{l+1/2}(t) \left[K^*_{l+1/2}(\lambda_1 t) - s_1^{l+1}t^{-l-1}K^*_{l+1/2}(\lambda_1 s_1) \right] dt; \tag{2.9}$$

$$\beta_{2l}(s_2) = - \chi_2 a_2 n_2 s_2^{-n_2} \int_0^{s_2} t^{n_2}I^*_{l+1/2}(t) \left[I^*_{l+1/2}(\lambda_2 t) - s_2^{-l}t^lI^*_{l+1/2}(\lambda_2 s_2) \right] dt,$$

$$h_i(r) = \chi_i r^{-1}U_{il}(r) \partial z_{i0}/\partial r, \quad W = \pi/(2s_ir^2) \tag{2.10}$$

(W represents the Wronskian functions $K^*_{\ell+1/2}(s_ir)$ and $I^*_{\ell+1/2}(s_ir)$, while $C_{1\ell}$ and $C_{2\ell}$ are arbitrary constants).

Let us examine boundary conditions (1.5)-(1.8). Subjecting Eq. (1.7) to the operation $(\sin \theta)^{-1}(\partial/\partial\theta)\sin \theta$, and Eq. (1.8) to the operation $(\sin \theta)^{-1}\partial/\partial\varphi$ and adding the resulting expressions, with allowance for continuity equation (1.2), we find

$$\gamma_0 \frac{\partial}{\partial t} \frac{\partial}{\partial r} (r^2u_1) = m_1 \left[L^2u_1 - \frac{\partial}{\partial r} \frac{1}{r} \frac{\partial}{\partial r} (r^2u_1) + \frac{\partial}{\partial r} (r^2u_1) \right] - \tag{2.11}$$

$$- m_2 \left[L^2u_2 - \frac{\partial}{\partial r} \frac{1}{r} \frac{\partial}{\partial r} (r^2u_2) + \frac{\partial}{\partial r} (r^2u_2) \right] + M_1L^2\gamma_1 + M_2L^2\gamma_2 - \varkappa_1L^2 \frac{\partial}{\partial r} (r^2u_1) - 2\varkappa_2 \frac{\partial}{\partial r} (r^2u_1).$$

We present the perturbations of the surface concentrations of the reactants in the form

$$\gamma_i = \sum_{l=1}^{\infty} \Gamma_{il}Y_l(\theta, \varphi) e^{\omega t}.$$

Inserting this expression and (2.4), (2.7) into (1.6) and using Eqs. (2.5) and the recursion formulas for the functions $I^*_{\ell+1/2}(x)$ and $K^*_{\ell+1/2}(x)$, we obtain a linear homogeneous system of algebraic equations to determine the constants $B_{i\ell}$, $\Gamma_{i\ell}$, and $C_{i\ell}$:

$$||a_{ij}||E^T = 0, \quad E = (B_{1l}, B_{2l}, \Gamma_{1l}, \Gamma_{2l}, C_{1l}, C_{2l}), \tag{2.12}$$
$$a_{11} = q_1K^*_{l-1/2}(q_1), \quad a_{12} = q_2I^*_{l+3/2}(q_2),$$

$$a_{21} = q_1K^*_{l-1/2}(q_1)(\gamma_0\omega + 2m_1 + \varkappa_1l(l+1) - 2\varkappa_2) + m_1q_1^2K^*_{l+1/2}(q_1), \quad a_{22} =$$
$$= q_2I^*_{l+3/2}(q_2)2m_2 - m_2q_2^2I^*_{l+1/2}(q_2), \quad a_{23} = M_1l(l+1), \quad a_{24} = M_2l(l+1),$$
$$a_{31} = \gamma_{10}q_1K^*_{l-1/2}(q_1) - b_{12}\beta_{1l}(s_1) I^*_{l+1/2}(s_1), \quad a_{33} = \omega + \chi_{s1}^{-1}l(l+1) +$$
$$+ f_{11} - b_{11}, \quad a_{34} = f_{12} - b_{12}, \quad a_{35} = - b_{12}K^*_{l+1/2}(s_1), \quad a_{41} = \gamma_{20}q_1K^*_{l-1/2}(q_1),$$

$$a_{42} = -b_{22}\beta_{2l}(s_2)K_{l+1/2}^*(s_2), \quad a_{43} = f_{21} - b_{21}, \quad a_{44} = \omega + \chi_{s2}^{-1}l(l+1) + f_{22} -$$

$$- b_{22}, \quad a_{46} = -b_{2z}I_{l+1/2}^*(s_2), \quad a_{51} = \beta_{1l}(s_1)[b_{1z}I_{l+1/2}^*(s_1) + d_1(s_1I_{l+3/2}^*(s_1) +$$

$$+ lI_{l+1/2}^*(s_1))], \quad a_{53} = b_{11}, \quad a_{54} = b_{12}, \quad a_{55} = b_{1z}K_{l+1/2}^*(s_1) - d_1(s_1K_{l-1/2}^*(s_1) +$$

$$+ (l+1)K_{l+1/2}^*(s_1))], \quad a_{63} = b_{21}, \quad a_{64} = b_{22}, \quad a_{66} = b_{2z}I_{l+1/2}^*(s_2) -$$

$$- d_2(s_2I_{l+3/2}^*(s_2) + lI_{l+1/2}^*(s_2)) \text{ (the remaining elements are zero).}$$

Equating the determinant of system (2.12) to zero, we have the sought characteristic equation. The complete solution of this equation can be obtained only by numerical means on a computer. We will restrict ourselves here to study of the states with neutral stability, without oscillations, and we will analyze several important limiting cases.

3. To find conditions of the existence of neutral, nonoscillatory states, we set the imaginary part of the roots of the equation $\Delta(\omega) \equiv \det||a_{ij}|| = 0$ equal to zero: Im $\omega = 0$, and we proceed to the limit Re $\omega \to 0$. Here, we divide the first column of the determinant $\Delta(\omega)$ by $q_1K_{l-1/2}^*(q_1)$, the second by $q_2I_{l+3/2}^*(q_2)$, the fifth by $K_{l+1/2}^*(s_1)$, and the sixth by $I_{l+1/2}^*(s_2)$ and we pass to the limit $\omega \to 0$, $s_i \to 0$, $q_i \to 0$, $q_i/s_i = \lambda_i = $ const. Using the properties of the functions $K_{l+1/2}^*(x)$, $I_{l+1/2}^*(x)$, we find

$$\lim_{x\to 0} \frac{xK_{l+1/2}^*(x)}{K_{l-1/2}^*(x)} = 2l - 1, \quad \lim_{s_1,q_1\to 0} \frac{\beta_{1l}(s_1)I_{l+1/2}^*(s_1)}{q_1K_{l-1/2}^*(q_1)} = -\chi_1a_1n_1\varphi_{l1},$$

$$\lim_{x\to 0} \frac{xI_{l+1/2}^*(x)}{I_{l+3/2}^*(x)} = 2l + 3,$$

$$\lim_{s_2,q_2\to 0} \frac{\beta_{2l}(s_2)K_{l+1/2}^*(s_2)}{q_2I_{l+3/2}^*(q_2)} = \chi_2a_2n_2\varphi_{l2},$$

$$\varphi_{l1} = [(2l+1)(2l+n_1+1)(2l+n_1-1)]^{-1},$$

$$\varphi_{l2} = [(2l+1)(2l+n_2+1)(2l+n_2+3)]^{-1}.$$

After some transformations, we reduce the equation of neutral stability to the form

$$\begin{vmatrix} \gamma_0 + \mu_l & M_1l(l+1) & M_2l(l+1) \\ \gamma_{10} - B_1 & f_{11} + A_{11} & f_{12} + A_{12} \\ \gamma_{20} - B_2 & f_{21} + A_{21} & f_{22} + A_{22} \end{vmatrix} = 0, \quad (3.1)$$

$$A_{ij} = b_{ij}\frac{d_i(l+\delta_{1i})}{b_{iz} - d_i(l+\delta_{1i})} + \chi_{si}l(l+1)\delta_{ij},$$

$$B_i = p_i\varphi_{li}b_{iz}\frac{d_i(2l+1)}{b_{iz} - d_i(l+\delta_{1i})}, \quad \mu_l = (m_1 + m_2)(2l+1) + \varkappa_1l(l+1) - 2\varkappa_2$$

(δ_{ij} is the Kronecker symbol). Here, the terms f_{ij} characterize the surface chemical reaction; A_{ij} characterize the combined effect of adsorption and diffusion of the substance from the volumes of the phases; B_i characterize adsorption and convective diffusion in the volumes of the phases. It is evident from the structure of the expressions for A_{ij} and B_i that with large values of d_i (large diffusion coefficients) for high-mode perturbations ($l \gg 1$), it is impossible to ignore the finiteness of adsorption rate.

Let us examine the case of a single substance in more detail. From (3.1) we have

$$f = -A + Ml(l+1)(\gamma_0 - B)/(\gamma_0 + \mu_l) \quad (3.2)$$

(the subscripts with f, A, and B have been dropped).

Equation (3.2) is a generalization of the relation obtained in [4] with allowance for the finite rate of adsorption and the existence of an initially nonuniform concentration profile in both phases. It can be examined as the condition for the critical chemical coefficient f. It is evident that since $\partial J/\partial\Gamma_i < 0$, $\partial J/\partial C_i > 0$, then $b_{ij} < 0$, $b_{iz} < 0$, $A > 0$, where the sign of B depends on the direction from which the substance is transported to the drop: sign $B_i = $ sign p_i. It follows from (3.2) that for hydrodynamic instability to occur, the critical value of the coefficient f must be negative and its modulus must exceed a certain value determined by the diffusion, adsorption, and surface activity of the reactants and the stationary concentration profile. The following conclusions can be made as a result of analysis of Eq. (3.2):

a. Let there be no initial concentration profile in the volume: $B = 0$. Then the fact that the reacting substance is charcterized by surface activity ($M < 0$) makes the system more stable. In fact, in this case, the condition of purely chemical instability $f + A < 0$ is replaced by condition (3.2). Meanwhile, the critical value of the chemical coefficient f increases in terms of its modulus. Purely chemical instability means that small perturbations of the volumetric and surface concentrations increase because the rate of the interfacial reaction increases more slowly with an increase in reactant concentration than does the supply of the substance to the interface.

b. Let there be an initially nonuniform concentration profile: $B \neq 0$. Then the critical value of f depends appreciably on the sign and magnitude of B. In the case when the inertia of the substance at the interface can be ignored ($\gamma_0 = 0$), we have $f = -A - M\ell(\ell + 1)B/\mu_\ell$. Thus, if the substance is surface-active and is transported to the surface of the drop ($B > 0$), then the modulus of the critical value of f decreases, i.e., the system becomes more unstable. Conversely, if the substance is removed from the drop ($B < 0$), then the system is stabilized.

c. Since B depends on ℓ, then at $\gamma_0 \neq 0$ the activity of the surface will have different effects on the stability of the system for different harmonics: at $\gamma_0 - B > 0$, the system will be stabilized; at $\gamma_0 - B < 0$, the system will be destabilized.

d. If the rate of adsorption is high (i.e., if adsorptive equilibrium takes place), then $A \sim (b_{ij}/b_{iz})d_i(\ell + \delta_{1i})$, and increases in proportion to ℓ. However, for a finite adsorption rate, exerting a large effect on the harmonics with large numbers, $A \to (-b_{ij}) = \text{const}$ and, thus, the instability threshold for f is reduced. This means that a finite adsorption rate destabilizes the system.

4. Let us examine the dispersion relation in an approximation in which we assume that the reaction is slow and that the drops are small, having two parameters: $\chi_i = a^2/D_i\tau \ll 1$, $R_i = a^2/v_i\tau \ll 1$. The remaining dimensionless parameters will be assumed to be quantities on the order of $O(1)$. It must be noted that if $d_i = (C_{i0}a/\Gamma_i^*)\chi_i^{-1} \sim O(1)$, then $C_{i0}a/\Gamma_i^* \sim \chi_i \ll 1$, which corresponds to the case of strong surfactants. Arranging the elements of the determinant in a series with respect to χ_i and R_i and discarding terms on the order of $O(1)$, we obtain the following characteristic equation from (2.12):

$$\begin{vmatrix} \gamma_0\omega + \mu_l & M_1 l(l+1) & M_2 l(l+1) \\ \gamma_{10} & \omega + f_{11} + A_{11} & f_{12} + A_{12} \\ \gamma_{20} & f_{21} + A_{21} & \omega + f_{22} + A_{22} \end{vmatrix} = 0, \tag{4.1}$$

which is cubic relative to ω and is still quite complicated to analyze; for a single substance, this equation takes the form

$$\gamma_0\omega^2 + [\gamma_0(f + A) + \mu_l]\omega + \mu_l(f + A) - \gamma_0 M l(l+1) = 0. \tag{4.2}$$

In accordance with the Rouse–Hurwitz criterion, all of the solutions of (4.2) have negative real parts only when

$$\gamma_0(f + A) + \mu_l > 0,$$
$$\mu_l(f + A) + \gamma_0|M| l(l+1) > 0. \tag{4.3}$$

Equation (4.2) has solutions with a nonvanishing imaginary part if its discriminant is less than zero:

$$D = (\gamma_0(f + A) - \mu_l)^2 - 4\gamma_0^2|M| l(l+1) < 0. \tag{4.4}$$

Inequalities (4.3), (4.4) make it possible to construct regions, in the coordinates (f, $|M|$), corresponding to different types of stability of the system (see Fig. 1). Broken line I in Fig. 1 separates the region of instability on the left from the region of stability located on the right of I. Each of these regions is in turn subdivided by the parabola II ($|M| = (\gamma_0(f + A) - \mu_\ell)^2/4\gamma_0^2\ell(\ell + 1)$) into two subregions: 1, 2, and 3, 4. Meanwhile, the inclined segment of the broken line touches the parabola at a point of discontinuity of the first derivative. Regions 2 and 3 correspond to unstable and stable regimes with oscillations, while there are no oscillations in regions 1 and 4.

It can be seen from the figure that one feature of the given system is the possibility of the development of instability only in the case $f < f_{cr} < 0$. Here, f_{cr} must exceed a critical value connected with the parameters of the adsorption-desorption and diffusion processes,
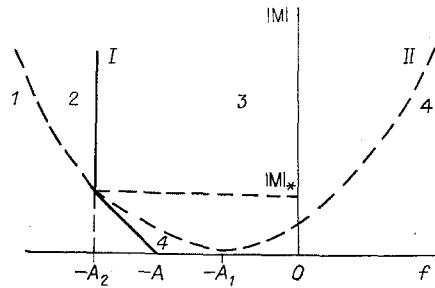
Fig. 1

as well as with the bulk and surface viscosities. It should also be noted that if instability is possible, it will occur at a value of $|M|$ as small as is desired. In other words, purely chemical instability, with as weak a connection with hydrodynamic instability as is desired ($|M| \neq 0$), leads to hydrodynamic instability. In the range $-A_2 \equiv -A - \mu_i/\gamma_0 < f < -A$, an increase in $|M|$ leads to stabilization of the system and the suppression of instability. At $f < -A - \mu_i/\gamma_0 \equiv -A_2$, the system turns out to be unstable with any value of $|M|$.

We should note one more interesting fact. If there is in general no connection with hydrodynamic instability ($|M| = 0$), then motion of the interface will not take place and we can speak only of chemical instability — which would be seen at $f < -A$. The presence of this coupling ($|M| \neq 0$) leads to a situation whereby stability also exists at $f < -A$, i.e., the stability threshold corresponding to f_{cr} increases in absolute value. Thus, it can be concluded that the Marangoni effects suppress chemical instability. All of the foregoing is true only for modes $\ell \geq 1$, since no hydrodynamic mode exists when $\ell = 0$ and, thus, the hydrodynamics of the system have no effect on its chemical stability.

Now let us examine the effect of finiteness of adsorption rate on the stability of the system. If adsorption is rapid and if there is equilibrium between the phase boundary and the regions adjacent to it, then $A \sim (b/b_z)d\ell$. If the adsorption rate is low, then $A \sim b = \text{const}$. An increase in ℓ is accompanied by a shift of the instability region to the left, in the direction of greater absolute values of f. Meanwhile, as can be seen from the expression for A, this shift is larger for rapid adsorption than for slow adsorption. This means that slow adsorption destabilizes the system.

It is interesting to follow the effect of dissipative processes (surface and bulk viscosities) on the stability characteristics of the system. The effects of dissipation are characterized by μ_ℓ. An increase in μ_ℓ is accompanied by a leftward shift of the vertical part of the broken line I and an increase in the slope of its lower part. If $|M|$ is fixed and $|M| < |M|_* = \mu_\ell^2/\gamma_0^2\ell(\ell + 1)$, then an increase in μ_ℓ will be accompanied by a decrease in modulus of the critical value f_{cr} corresponding to the given value of $|M|$ and f_{cr} will approach $-A$, i.e., the system will become more unstable. If $|M| > |M|_*$, then f_{cr} will initially increase. Beginning with $\mu_\ell^2 = |M|\gamma_0^2\ell(\ell + 1)$, f_{cr} will then decrease in terms of its modulus. Thus, in a certain sense, an increase in the surface and bulk viscosities will lead to destabilization of the system. This conclusion — which at first glance seems paradoxical — proves to be natural for coupled oscillatory systems in general and has analogies in flutter theory and the theory of stability of Poiseuille flow, for example. The reason for this phenomenon is that the phase relations between perturbation modes are such that these perturbations draw on energy from an external source. In our case, this source was the flow of energy across the phase boundary. An increase in viscosity may make these relations more optimal from the viewpoint of the extraction of energy from the source and, thus, may serve to increase instability [10].

In conclusion, we note that it can be shown on the basis of analysis of Eq. (4.1) that for two reacting subtances, Marangoni effects may either destabilize a chemically stable system or stabilize a chemically unstable system, depending on the kinetics of interfacial processes.

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CASCADE TRANSFER OF ENERGY, VORTICITY, AND A PASSIVE IMPURITY IN HOMOGENEOUS
ISOTROPIC TURBULENCE (TWO- AND THREE-DIMENSIONAL)

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Unidimensional turbulence is modeled experimentally in flows behind a grid. An extensive amount of empirical data has been accumulated on this subject, but several problems arise in connection with its analysis. Of primary interest is the reason that different exponents n in exponential laws describing the decay of fluctuation energy $\langle u^2 \rangle \sim t^{-n}$ are obtained in different experiments (see [1], for example). It is believed that these differences are connected with the "initial" conditions (although the authors of [2] assert that the problem lies in the analysis itself). The more refined spectral characteristics of the velocity field (and the field regarding a passive impurity) also differ in different experiments [1, 3].

Recent investigations have also been concerned with quasi-two-dimensional turbulence realized (as hypothesized) in grid flows of a strongly conducting fluid in a strong transverse magnetic field [4-6]. The results of the experiments conducted here are also conflicting.

It is generally held that the first question that needs to be answered satisfactorily is the connection between the spectral characteristics (exponential asymptotes) and the exponent n in the exponential law of fluctuation energy decay $\langle u^2 \rangle$. The point is that $\langle u^2 \rangle$ is coarser than the spectrum, an experimental characteristic. Thus, its measurements are more reliable.

To establish such a connection, it is necessary to go outside the framework of the scale-invariant interval because, in the integral $\langle u^2 \rangle = \frac{2}{3} \int_0^\infty E(k)\,dk$, the range of values of k for which E(k) is known should be broad enough to obtain a good approximation of the entire integral [3]. As a result, it is necessary to determine additional features of the process of vortex breakup (combination).

A vortex of a certain scale can be subdivided into two, three, or more smaller vortices. We will assume that for each fixed scale (wave number k) there is a certain probable multiplicity of subdivisions α_k. Meanwhile, the smaller vortices into which the initial vortex is subdivided are of approximately the same dimensions. Since the process of vortex breakup (combination) occurs as a result of inertial effects, we will assume that the inertial interaction of the vortices is realized mainly during the subdivision (combination). As a result of formalization of this physical hypothesis, we obtain an equation for the spectral function of the velocity field which accounts for the spectral hypotheses of Kolmogorov—Obukhov (for three-dimensional turbulence) and Kraichnan—Batchelor (for two-dimensional turbulence). The